



The Effect of Electrolyte Additives Upon the Kinetics of Lithium Intercalation/De-Intercalation at Low Temperatures

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Outline

- **Introduction**
- **Background**
- **Evaluation of Lithium-Ion Electrolyte Additives**
 - *Vinylene carbonate (VC)*
 - **Alkyl pyrocarbonates (DMPC and DBPC)**
 - **Lithium methoxide (LiOCH₃)**
- **MCMB-LiNiCoO₂ experimental cell results**
 - Charge/discharge characteristics as a function of temperature
 - Electrochemical impedance spectroscopy (EIS) measurements
 - D.C. micropolarization measurements
 - Tafel polarization measurements
- **Conclusions**



Objective

- Develop low temperature electrolytes which will enable the operation of lithium-ion cells over a wide range of temperatures (-40° to $+40^{\circ}\text{C}$) for future Mars missions (enabling Landers and Rovers).

Approach

- Develop improved electrolyte formulations that possess high conductivity over a range of temperatures, good electrode passivation characteristics, and good electrochemical and chemical stability to enable the operation of lithium ion cell at temperatures as low as -50°C .
- Evaluate candidate electrolytes in experimental Li-carbon, Li-LiNiCoO₂, and MCMB-LiNoCoO₂ three-electrode cells (with psuedo Li reference).
- ***Investigate the viability of using electrolyte additives to improve the kinetics of lithium intercalation/de-intercalation (especially at low temperature).***



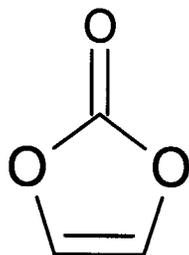
Background

- Researchers from SAFT have demonstrated improved performance of lithium-ion cells containing electrolytes with VC (decreased irreversible capacity losses, improved life characteristics, improved tolerance to high temperature exposure).
 - C. Jehoulet, P. Biensan, J.M. Bodet, M. Broussely, C. Moteau, C. Tessier-Lescourret, Proc. Electrochem. Soc. 97-18 (Batteries for Portable Application and Electric Vehicles), The Electrochem. Soc. Inc., Pennington, NJ (1997), pp. 974-985.
 - Using density functional theory calculations, researchers have studied the fundamental reductive decomposition reactions involved with the use of vinylene carbonate in lithium-ion battery environments.
 - Y. Wang, S. Nakamura, K. Tasaki, and P. B. Balbuena, *J. Amer. Chem. Soc.*, **2002**, 124, 4408-4421.
 - Using spectroscopic techniques, researchers have suggested that VC polymerizes on the lithiated graphite surfaces, forming poly alkyl Li-carbonate species that suppress both solvent and salt anion reduction. Aurbach and coworkers have also demonstrated that VC also interacts with cathode materials, and can result in better cathode kinetics (reduced impedances).
 - D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, and U. Heider, *Electrochim Acta.*, **2001**, xx, xxxx.

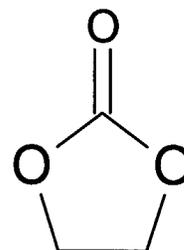


Background

- Vinylene carbonate (VC) is an unsaturated analogue to ethylene carbonate.



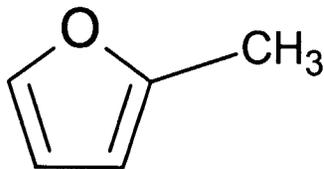
Vinylene carbonate (VC)



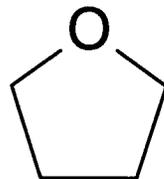
Ethylene carbonate (EC)

- A similar concept of using unsaturated analogues of oxygenated lithium-based electrolyte solvents was investigated in the context of Li-TiS₂ systems (i.e, the use of 2-methylfuran in THF/2-MeTHF-based solutions).

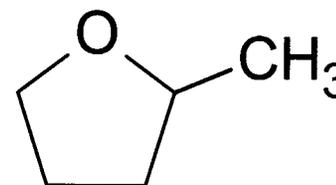
➤ *Abraham and coworkers (EIC)*



2-Methylfuran



Tetrahydrofuran (THF)



2-Methyltetrahydrofuran (THF)



Experimental MCMB-LiNi_{0.8}Co_{0.2}O₂ Carbon Cells

Electrolytes Selected for Evaluation in Experimental Cells

- 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:2 v/v)
- 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3 v/v)
- 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4 v/v)
- 1.0 M LiPF₆ EC+ DMC+EMC (15:15:70 v/v)
- 0.6 M LiPF₆ EC+DEC+DMC+EMC (1:3:3:3 v/v)



- 1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4 v/v)
- **1.0 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:4 v/v)**
+ 1.5% Vinylene Carbonate (VC)

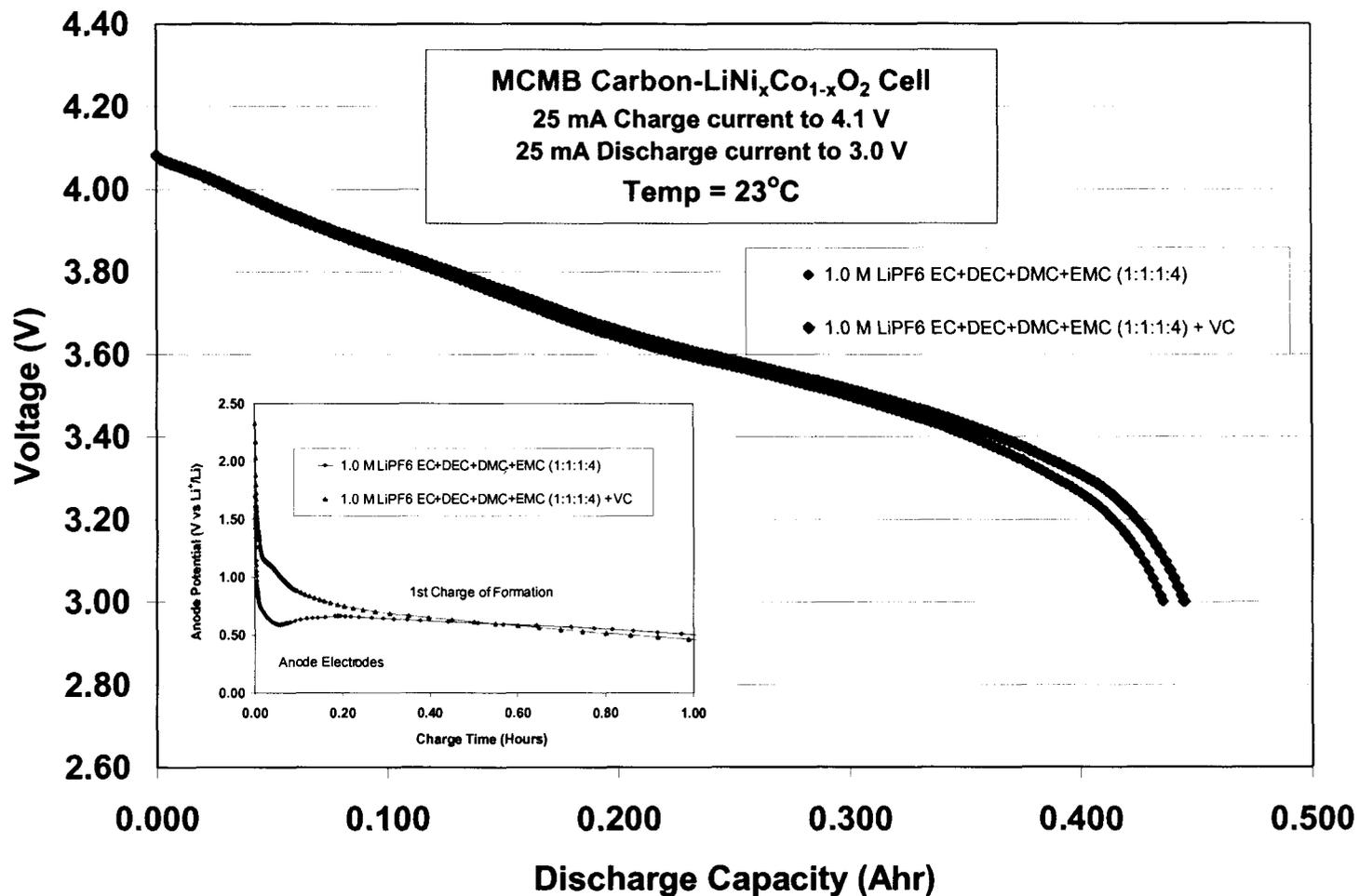
- MCMB Carbon-LiNiCoO₂ Cells
- 400-450 mAh Size Cells
- All Cells equipped psuedo Li metal reference electrodes
- Flooded electrolyte design (cylindrical cells)

Techniques Used to Study the Low Temperature Characteristics

- Charge/discharge behavior at various temperatures
- Electrochemical Impedance Spectroscopy (EIS)
- DC Polarization Techniques



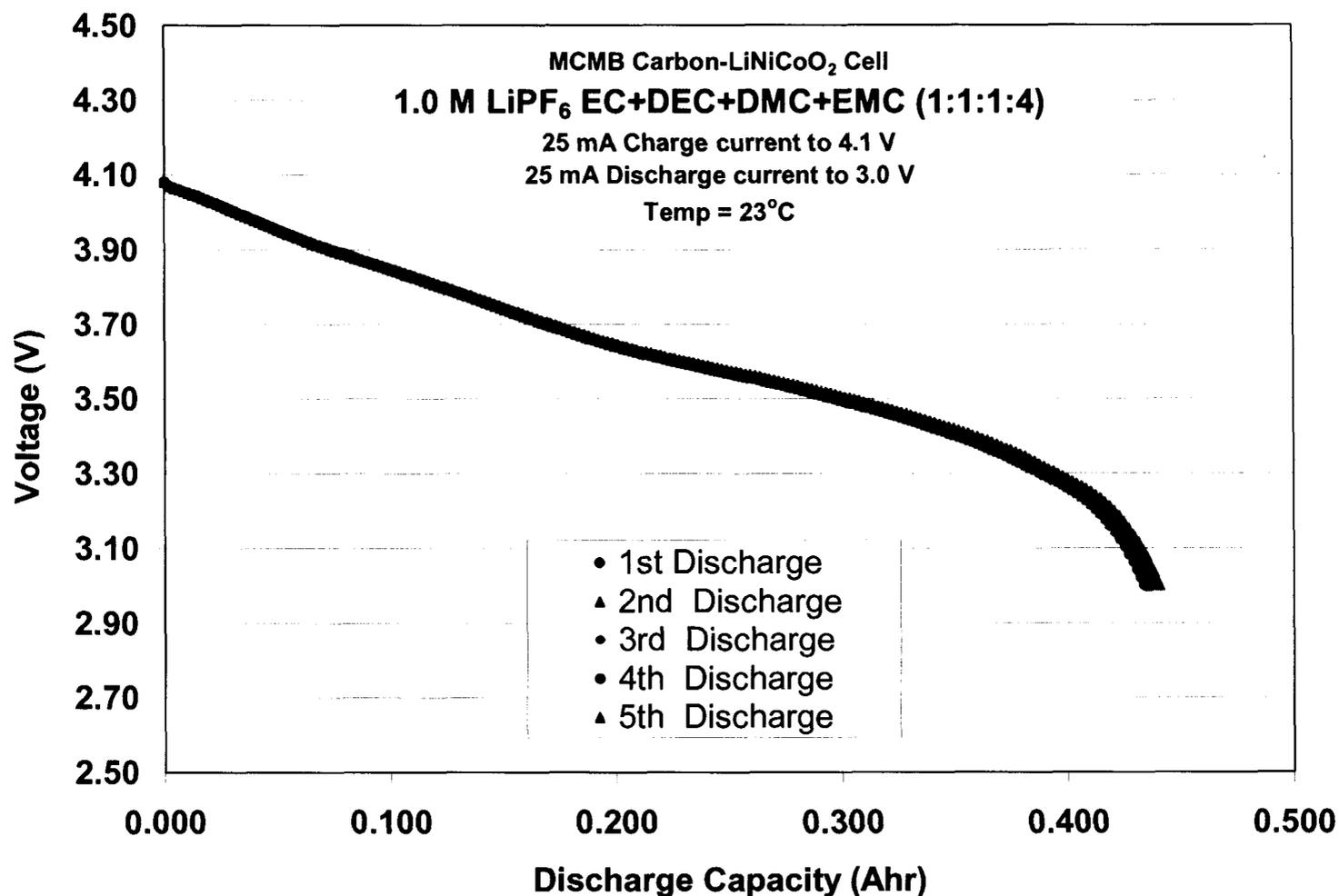
Effect of Electrolyte Additives on Cell Performance : Low Temperature Performance in Experimental MCMB-LiNi_xCo_{1-x}O₂ Cells Formation Characteristics





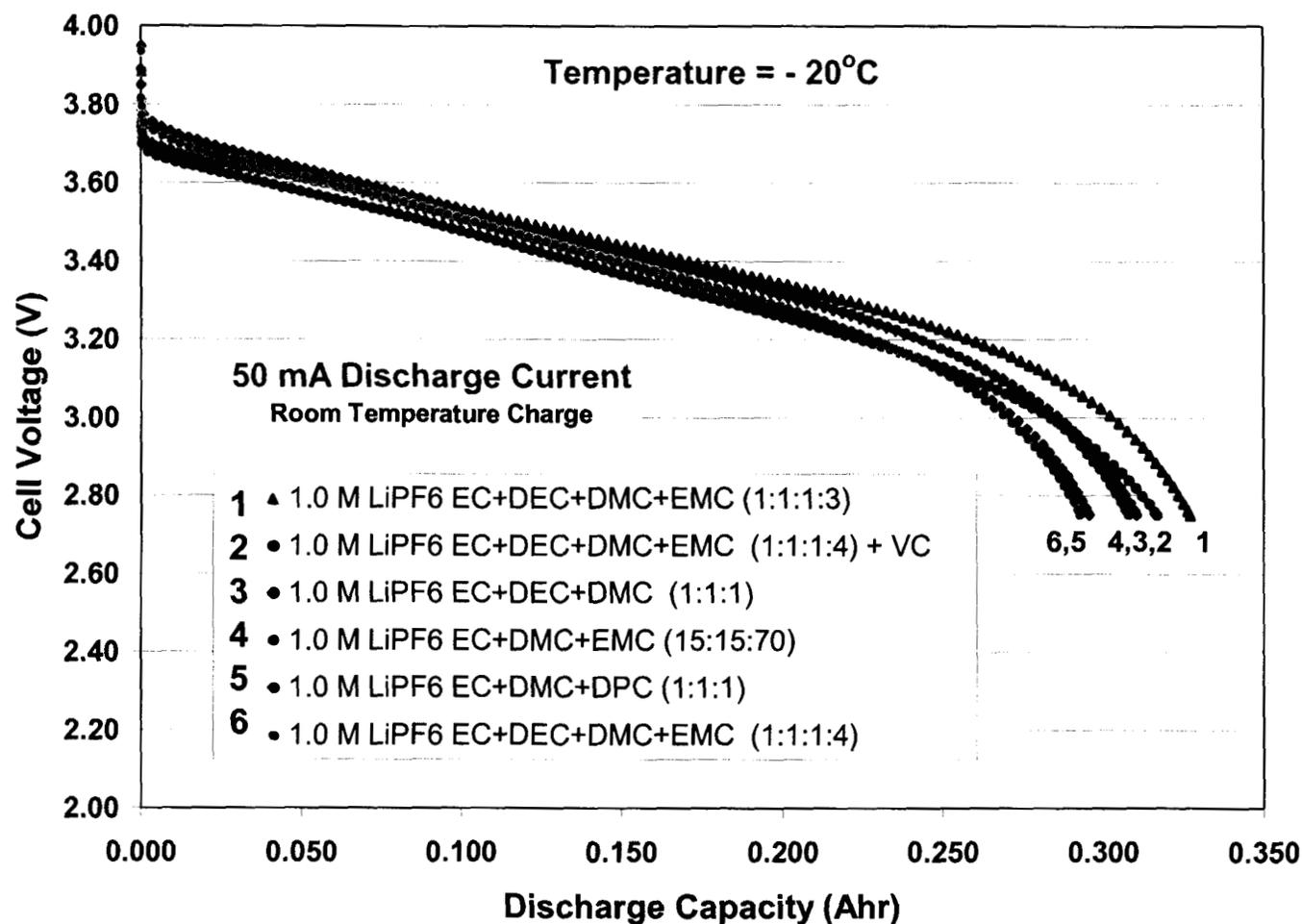
Formation Characteristics of MCMB-LiNiCoO₂ Experimental Cells

Evaluation of Quaternary Carbonate Low Temperature Electrolytes





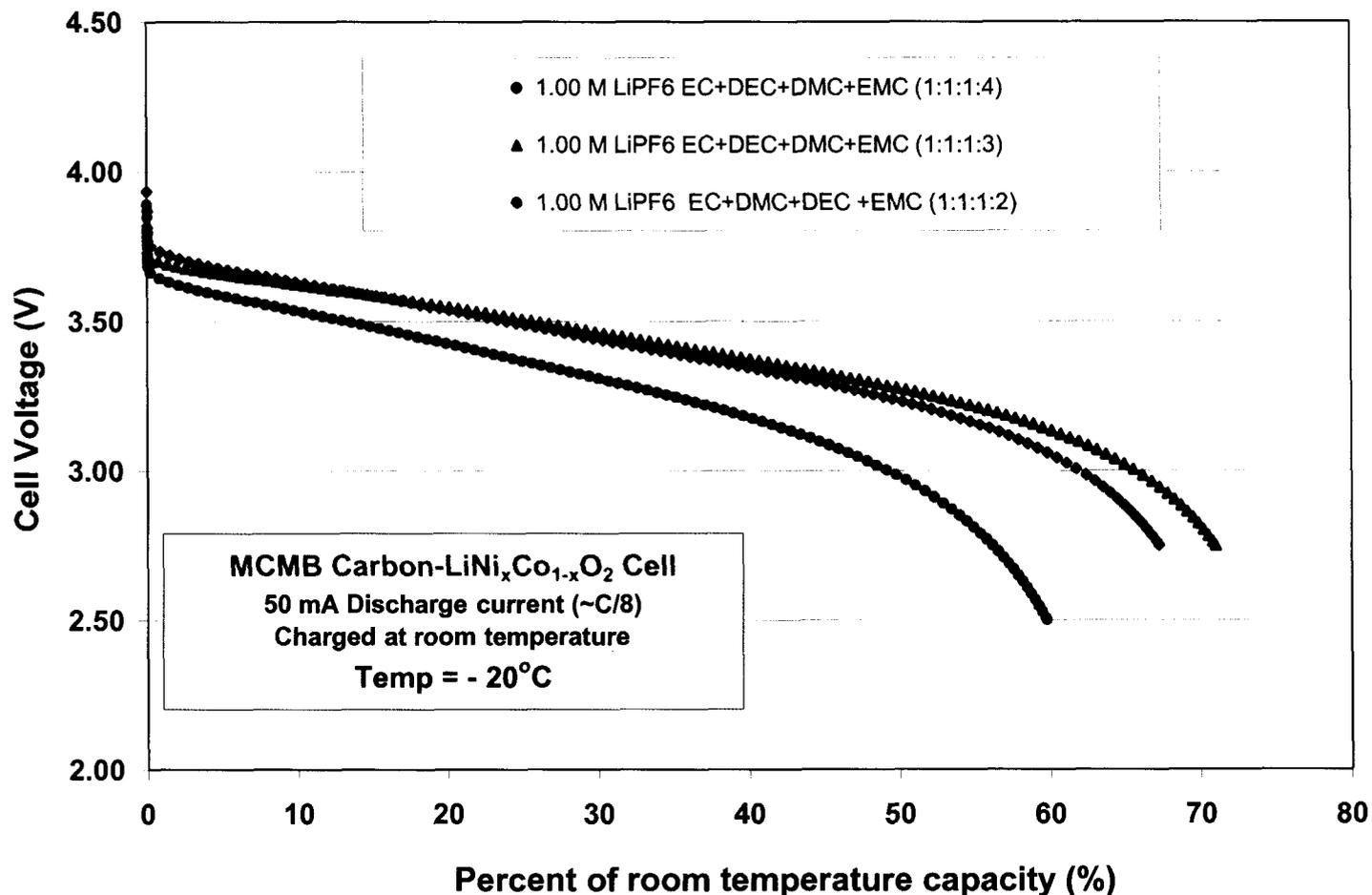
Low Temperature Performance of MCMB-LiNiCoO₂ Experimental Cells Effect of Electrolyte Upon Discharge Capacity at Low Temperature (-20°C)



- A number of low EC-content electrolytes have been shown to have good low temperature performance characteristics.



Effect of Electrolyte Additives on Cell Performance : Low Temperature Performance in Experimental MCMB-LiNi_xCo_{1-x}O₂ Cells

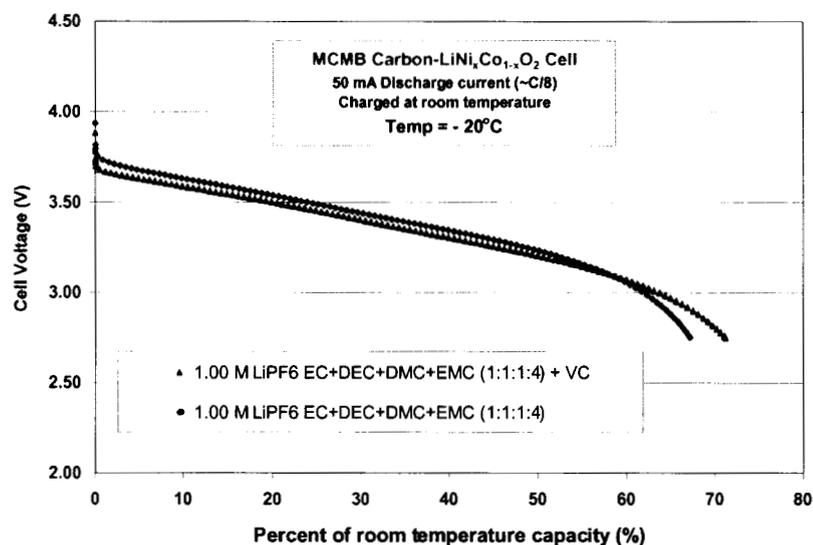


- Of the quaternary-based electrolytes, 1.0 M LiPF6 EC+DEC+DMC+EMC (1:1:1:3) was observed to display the best performance down to -50°C.

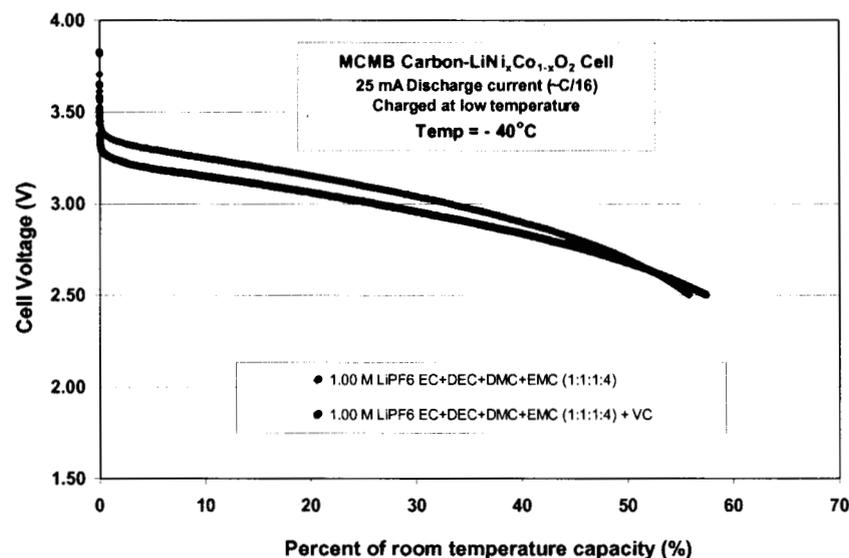


Effect of Electrolyte Additives on Cell Performance : Low Temperature Performance in Experimental MCMB-LiNi_xCo_{1-x}O₂ Cells Discharge Capacity at Low Temperature (RT Charge)

Temp = - 20°C (~C/8 Rate)



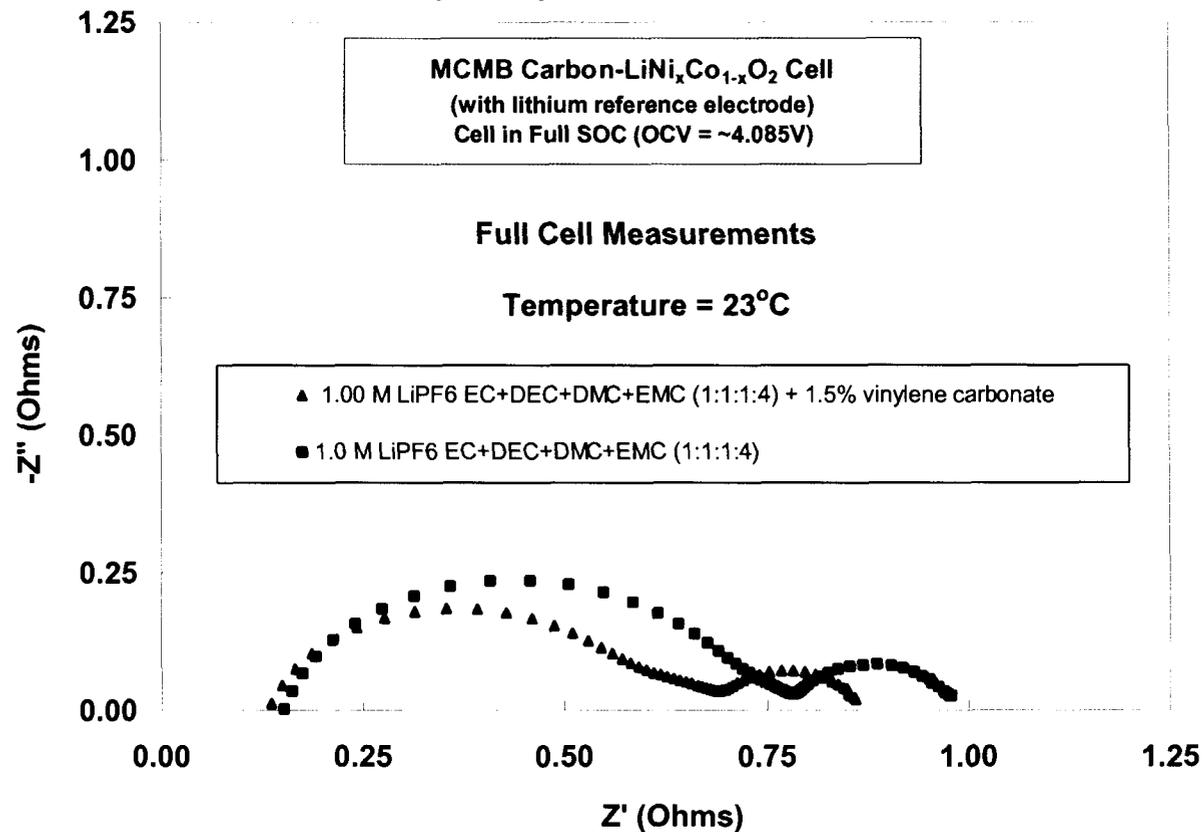
Temp = - 40°C (~C/16 Rate)



➤ When *vinylene carbonate (VC)* was added to a MCMB-LiNi_xCo_{1-x}O₂ cell containing a quaternary-based electrolyte, improved low temperature discharge capacity was observed at -20 and -40°C.



Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells EIS Measurements at 23°C (Full Cell) *Use of Vinylene Carbonate (VC)*



- The addition of *vinylene carbonate (VC)* was observed to result in lower film resistance, suggesting improved Li-ion migration through the electrode surface films.

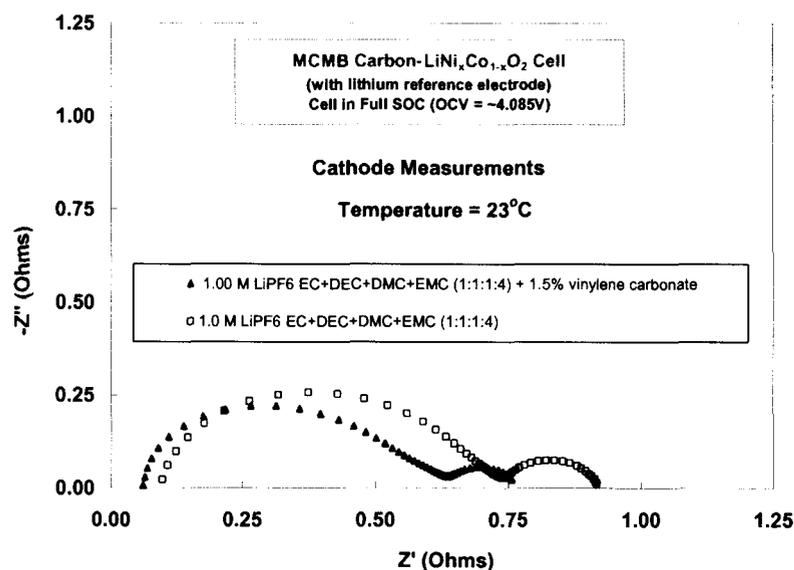


Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells

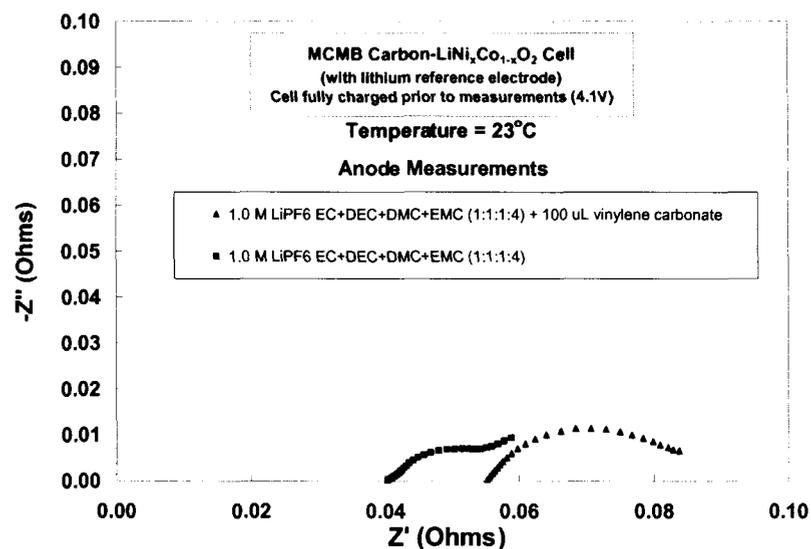
EIS Measurements at 23°C

Use of Vinylene Carbonate (VC)

Cathode Measurements



Anode Measurements



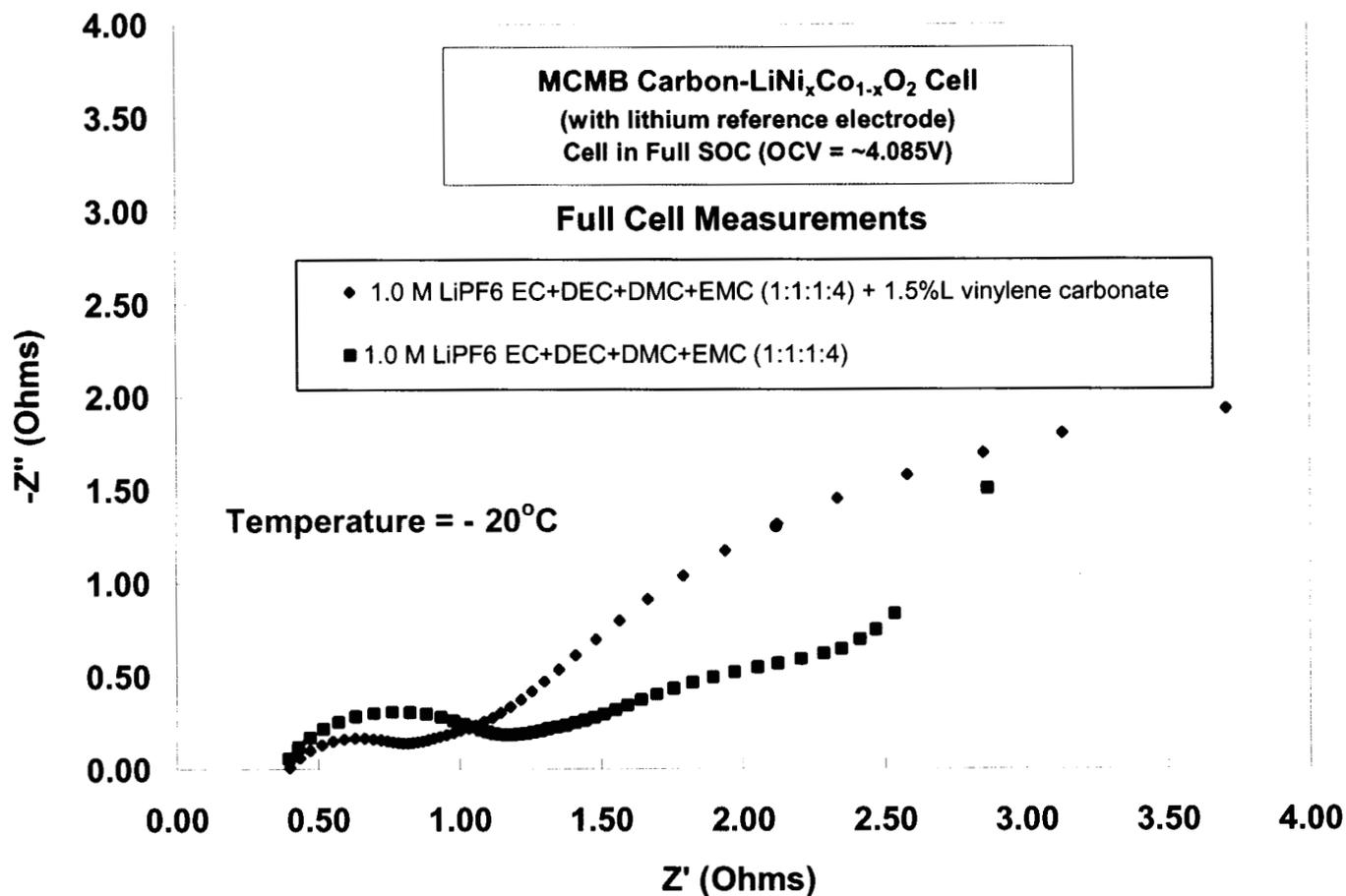
- When the impedance spectra were compared for each electrode, the cathode was observed to display lower film resistance values, whereas, the anode displays higher resistance.



Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells

EIS Measurements at -20°C (Full Cell)

Use of Vinylene Carbonate (VC)



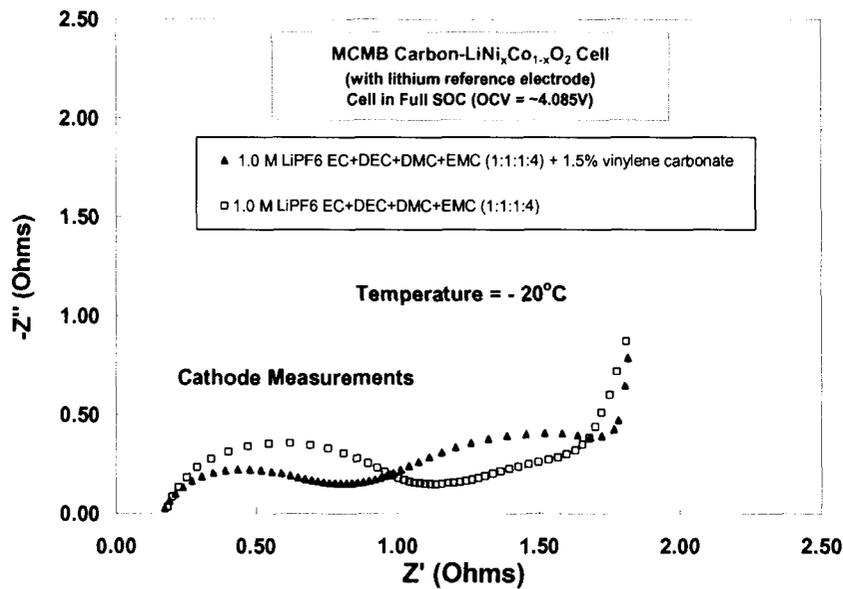


Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells

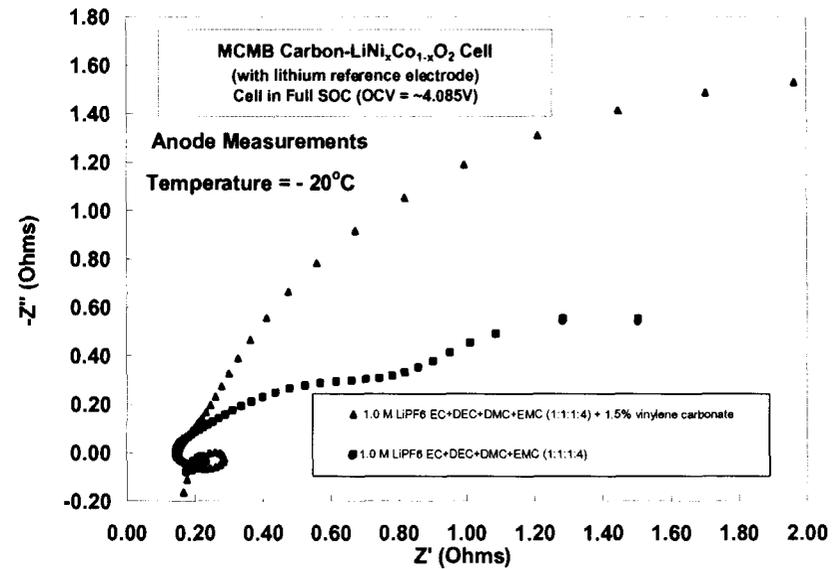
EIS Measurements at -20°C

Use of Vinylene Carbonate (VC)

Cathode Measurements



Anode Measurements

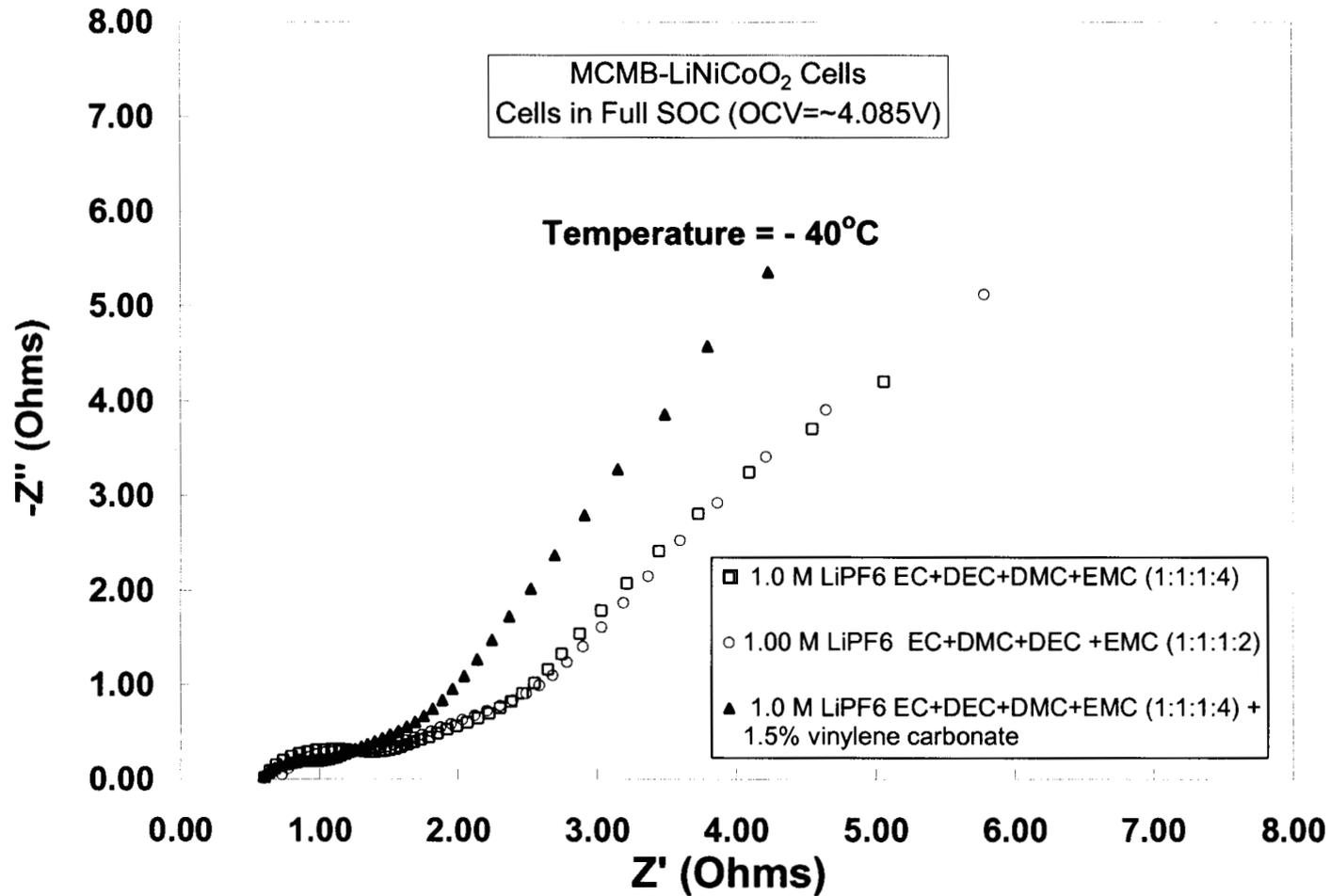




Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells

EIS Measurements at -40°C (Full Cell)

Use of Vinylene Carbonate (VC)



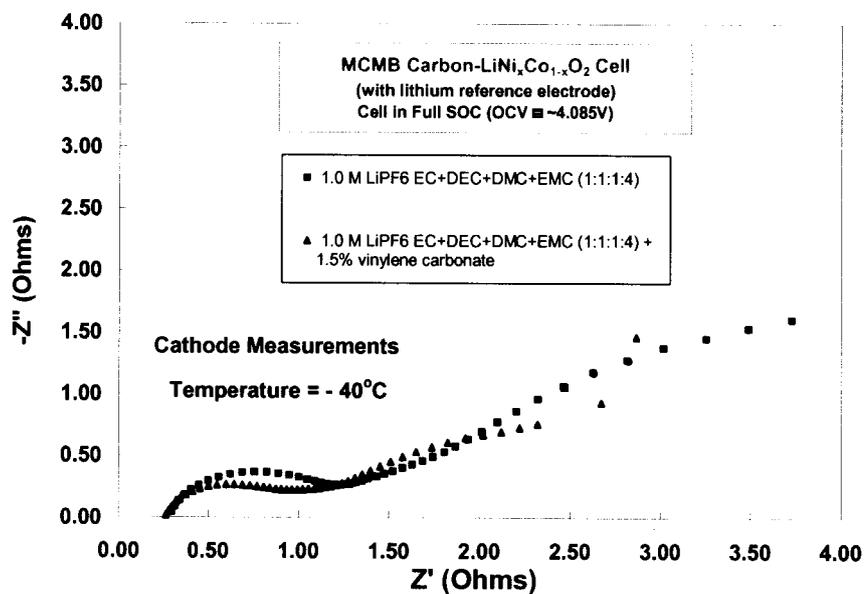


Effect of Electrolyte Additives Upon the Performance of Lithium-Ion Cells

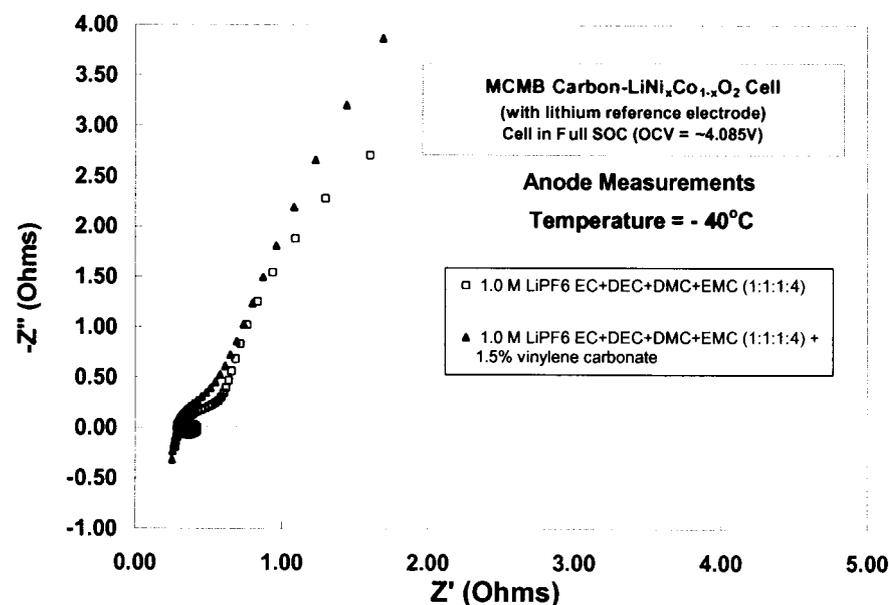
EIS Measurements at -40°C

Use of Vinylene Carbonate (VC)

Cathode Measurements

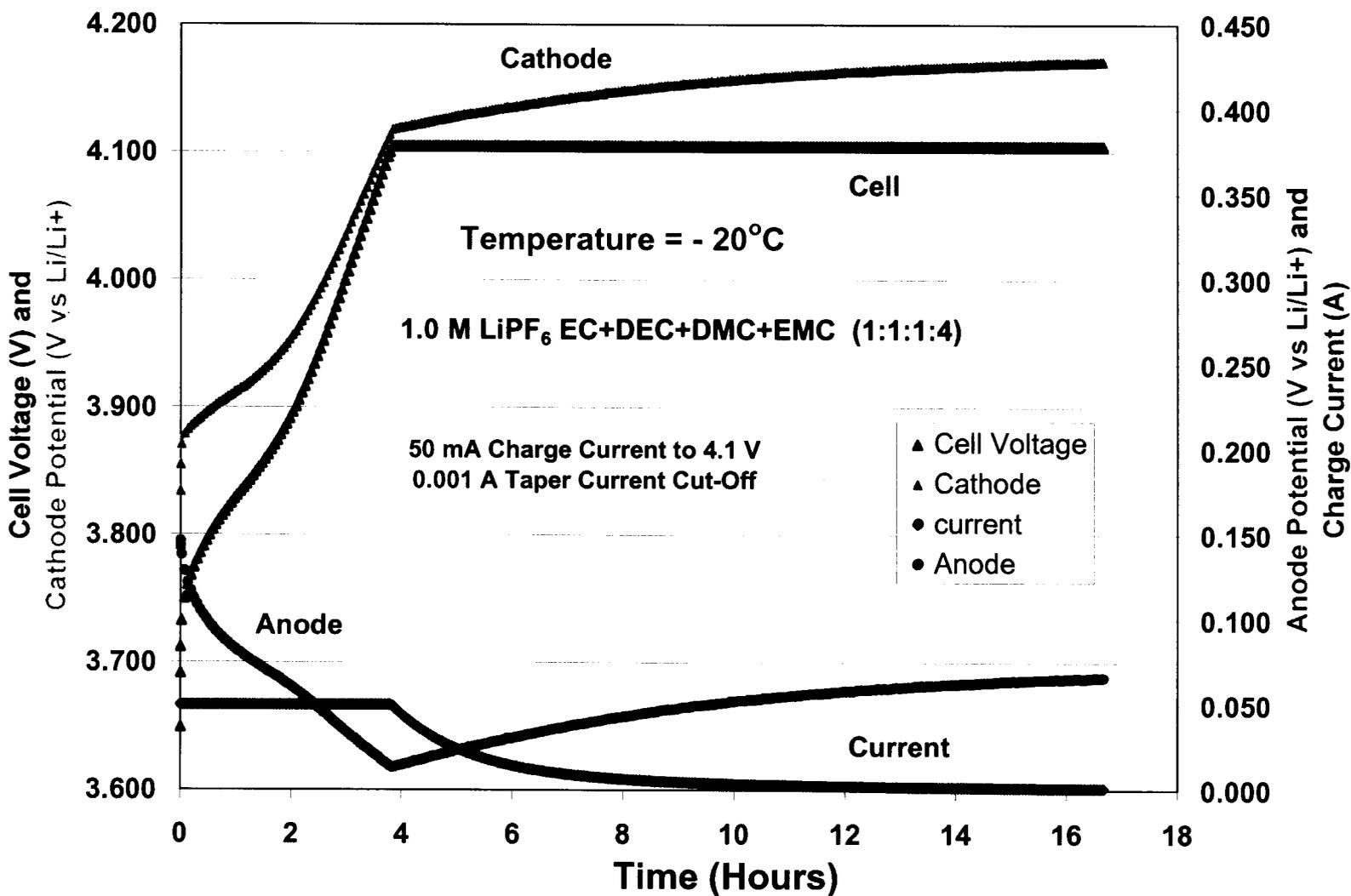


Anode Measurements



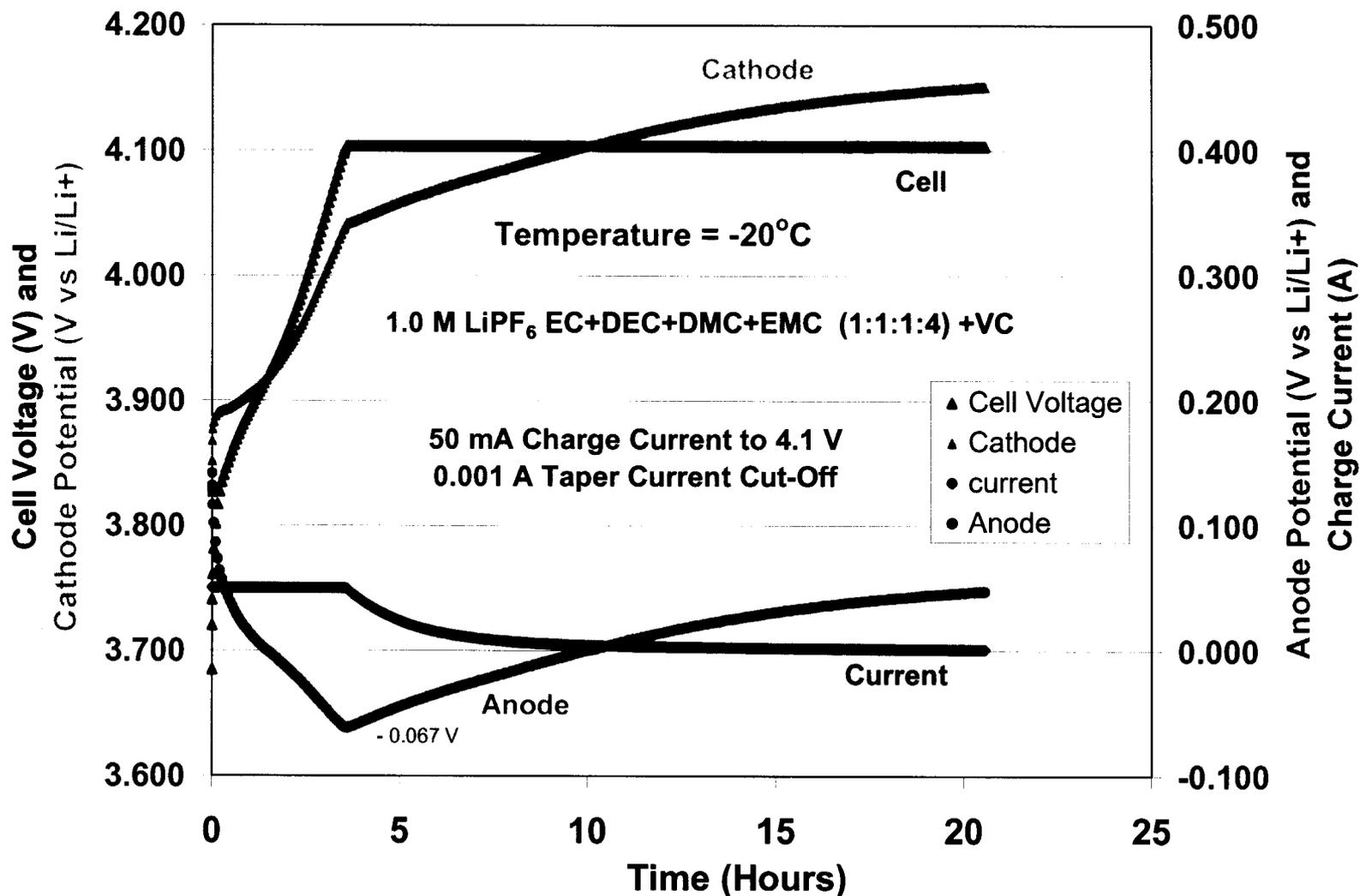


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-20°C)



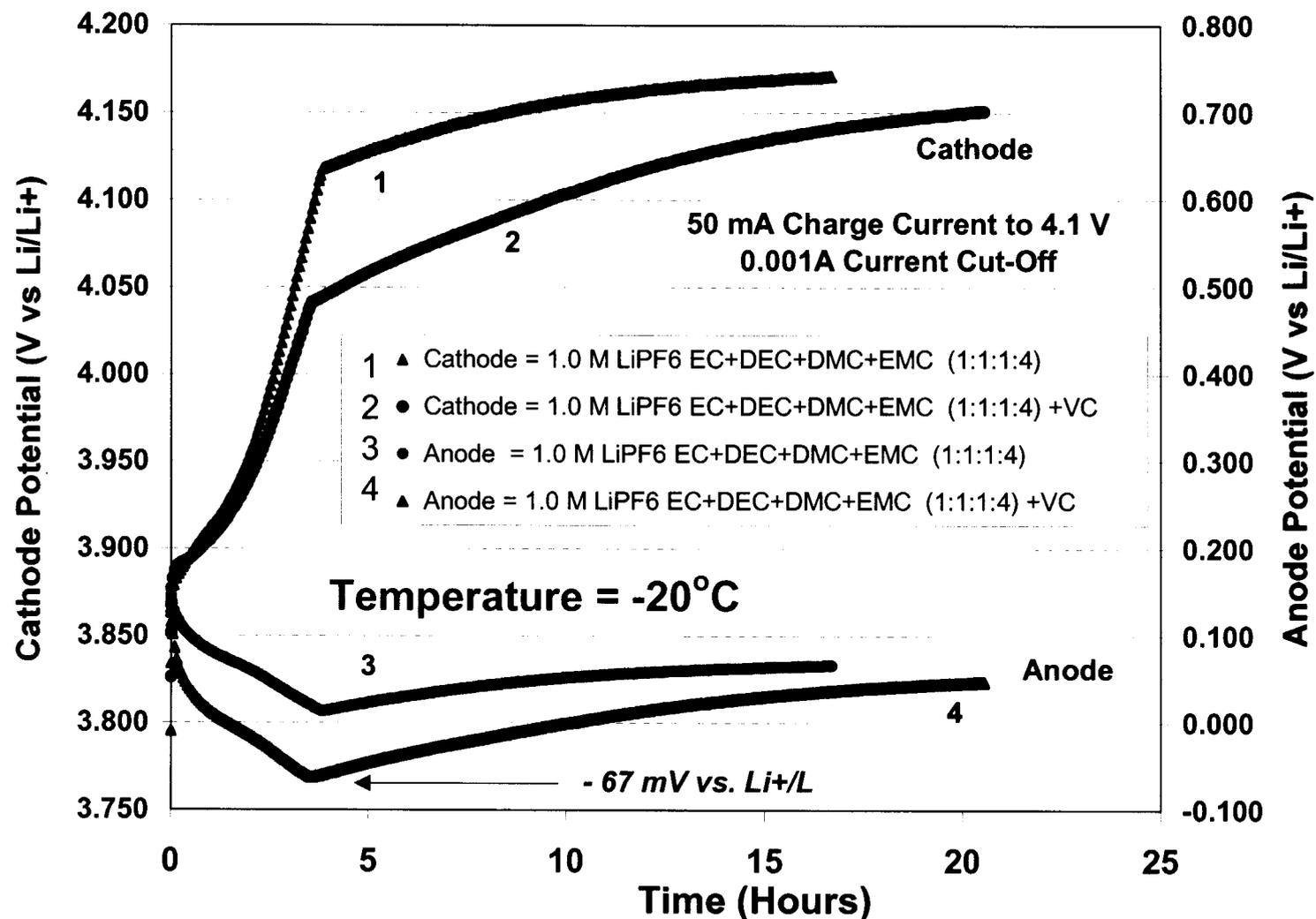


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-20°C)



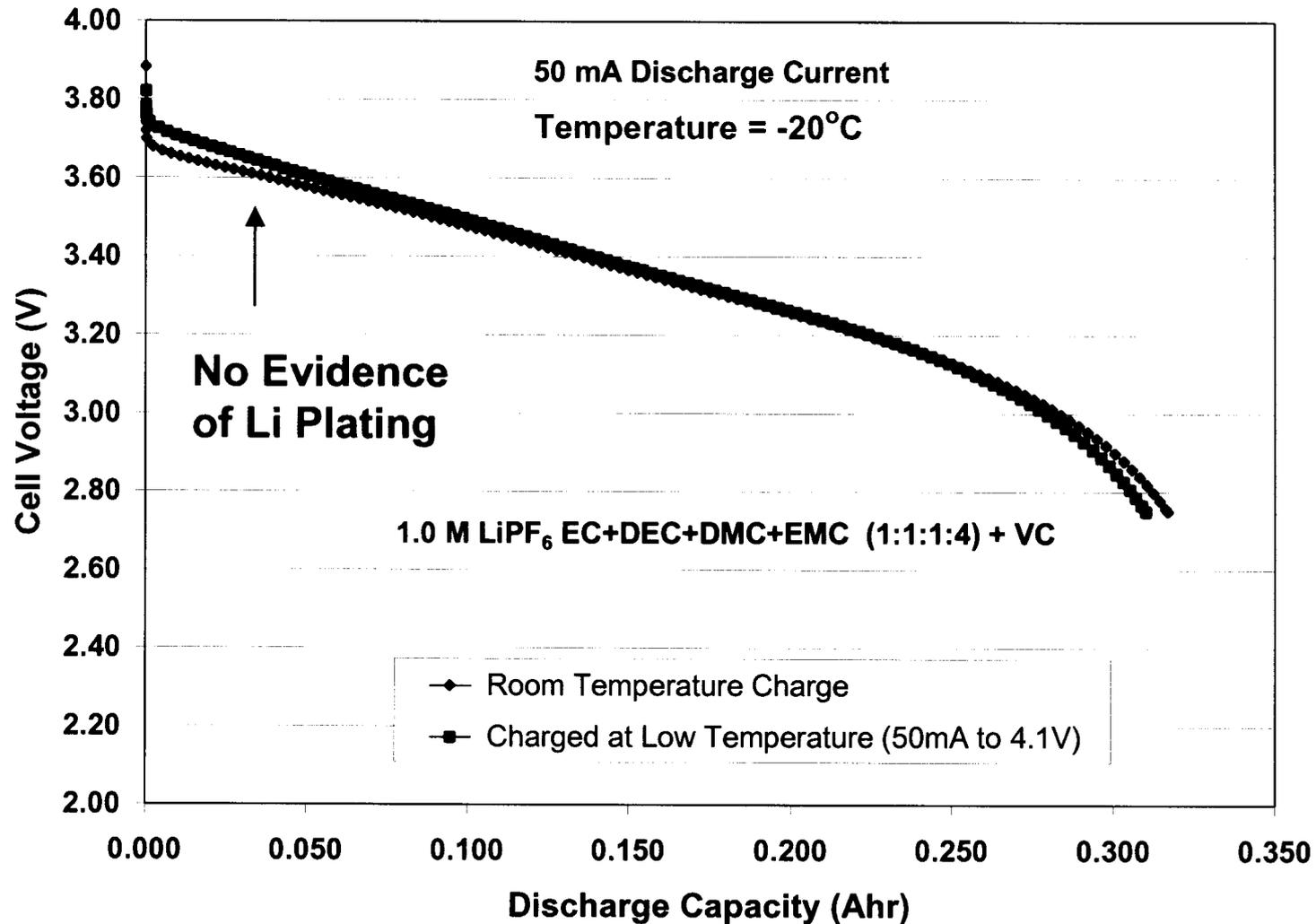


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (-20°C)



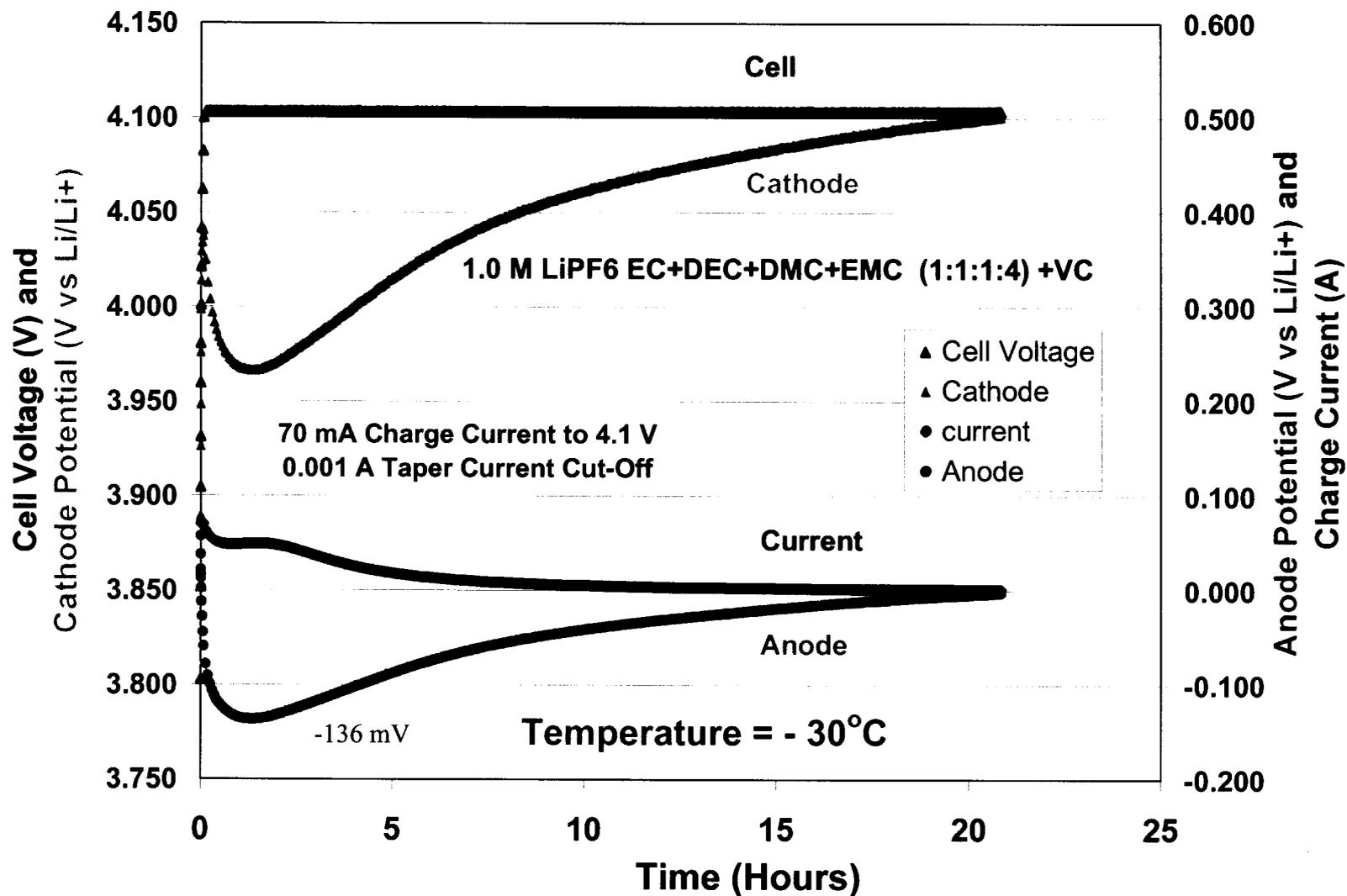


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Effect of Charging at Low Temperature (-20°C)



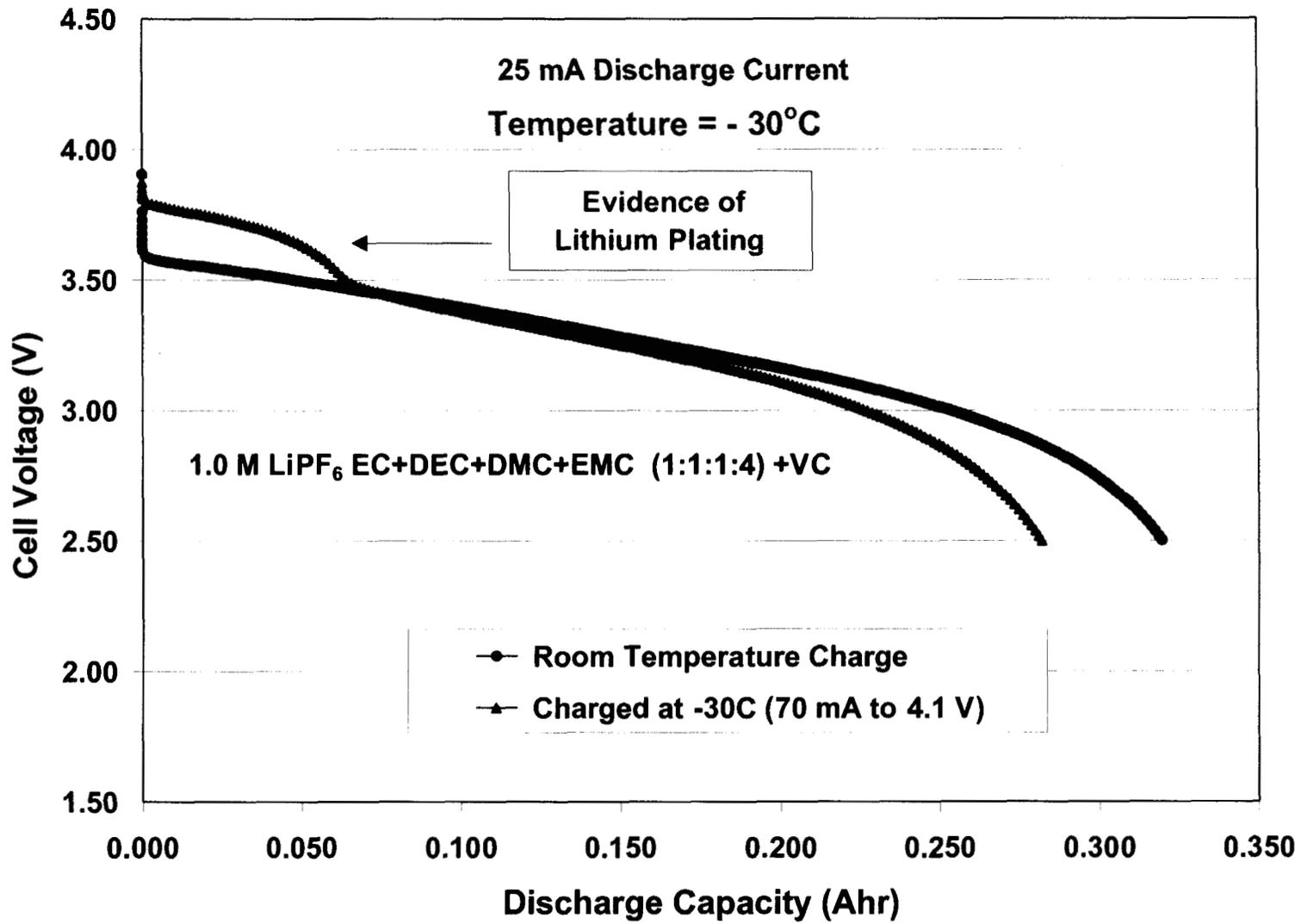


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (- 30°C)



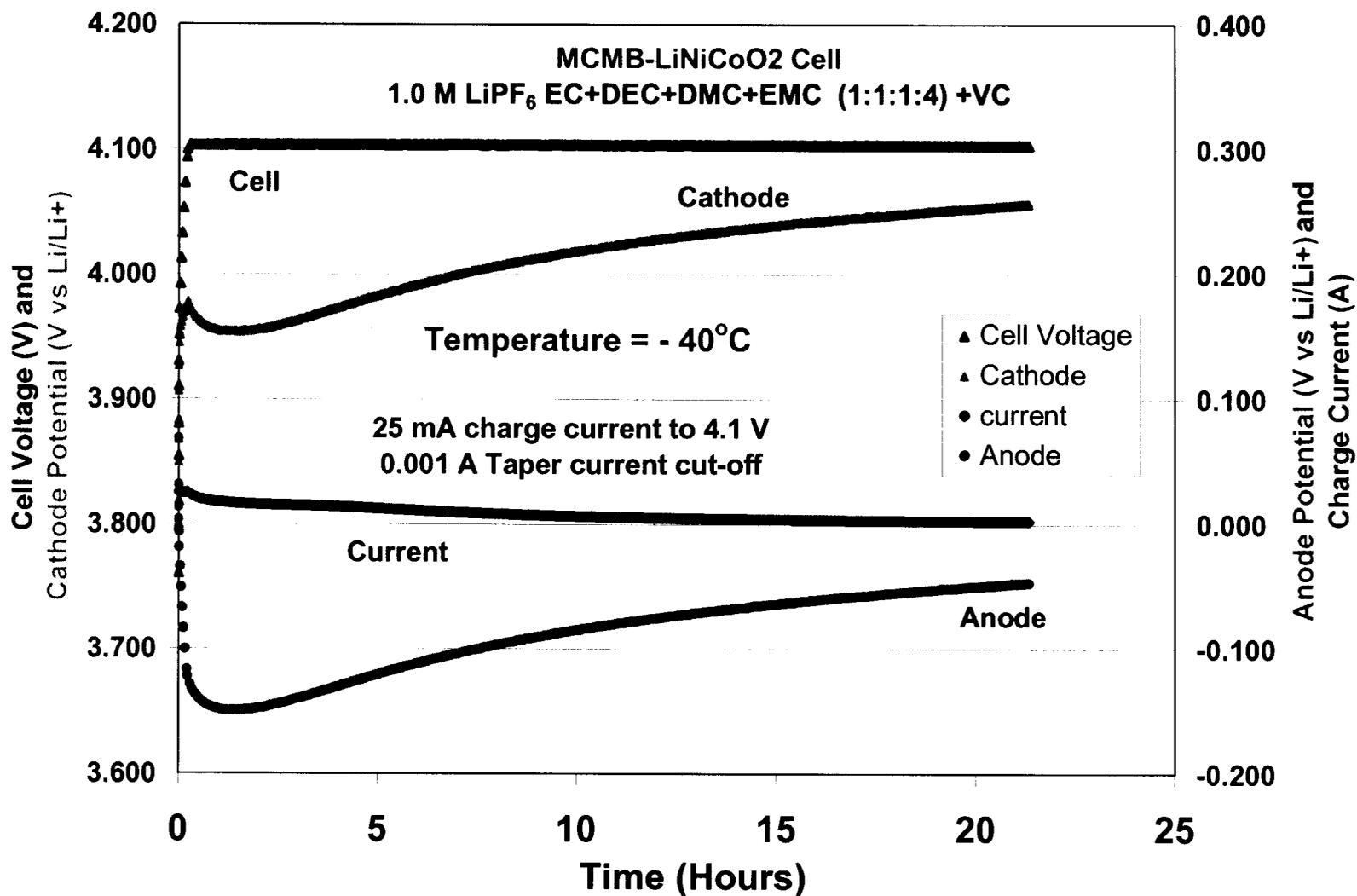


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Effect of Charging at Low Temperature (- 30°C)



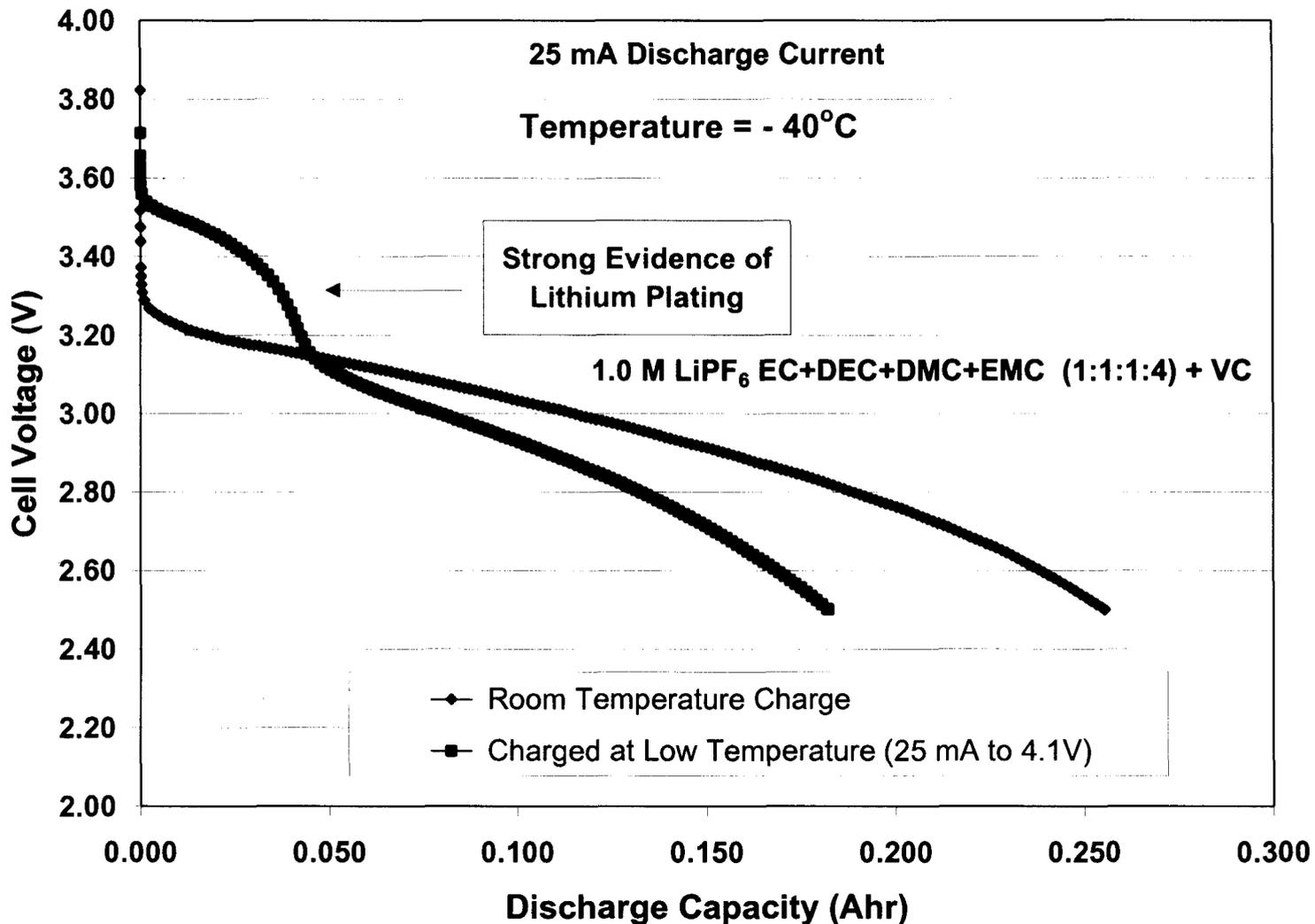


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (- 40°C)



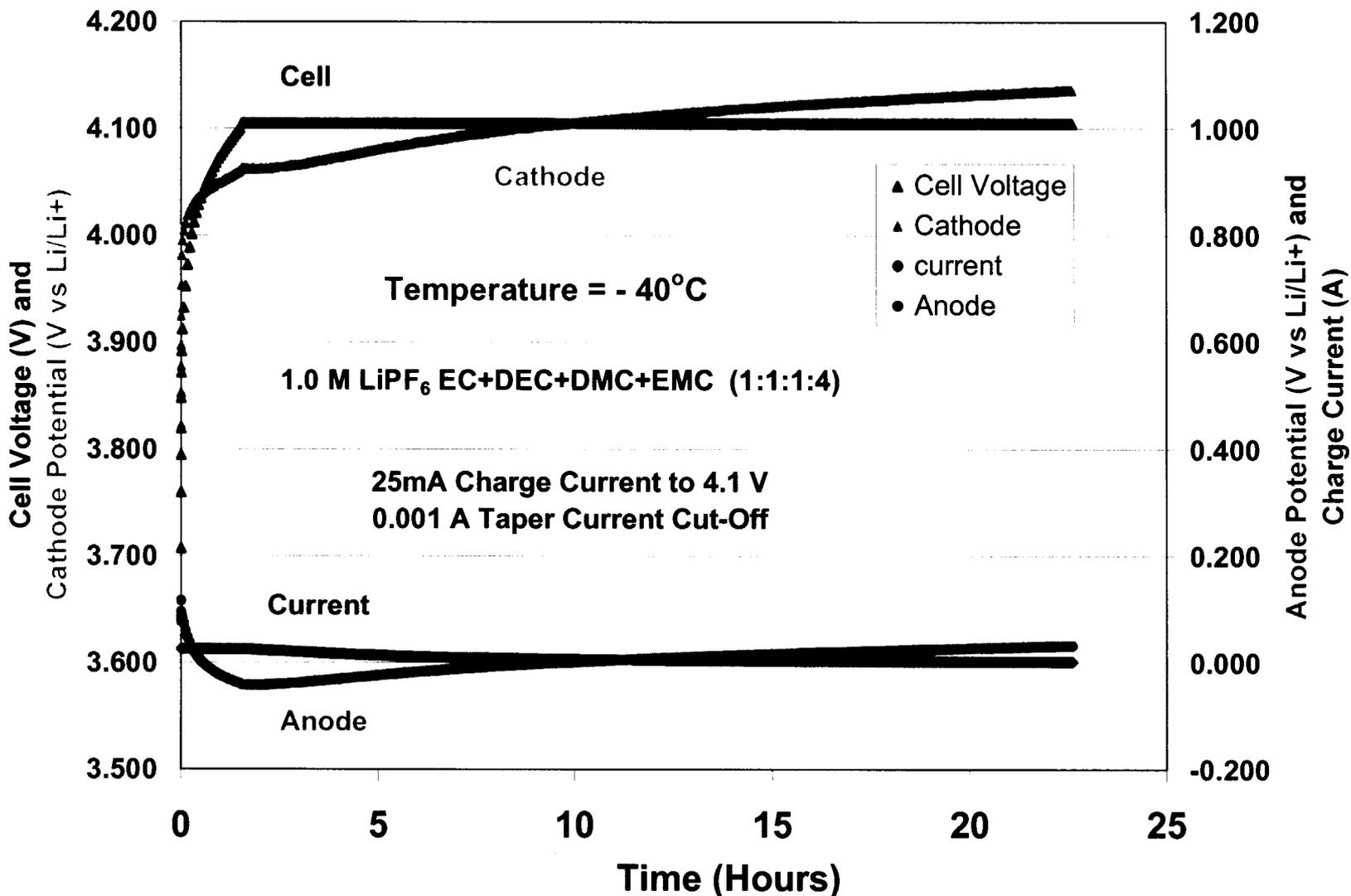


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Effect of Charging at Low Temperature (-40°C)



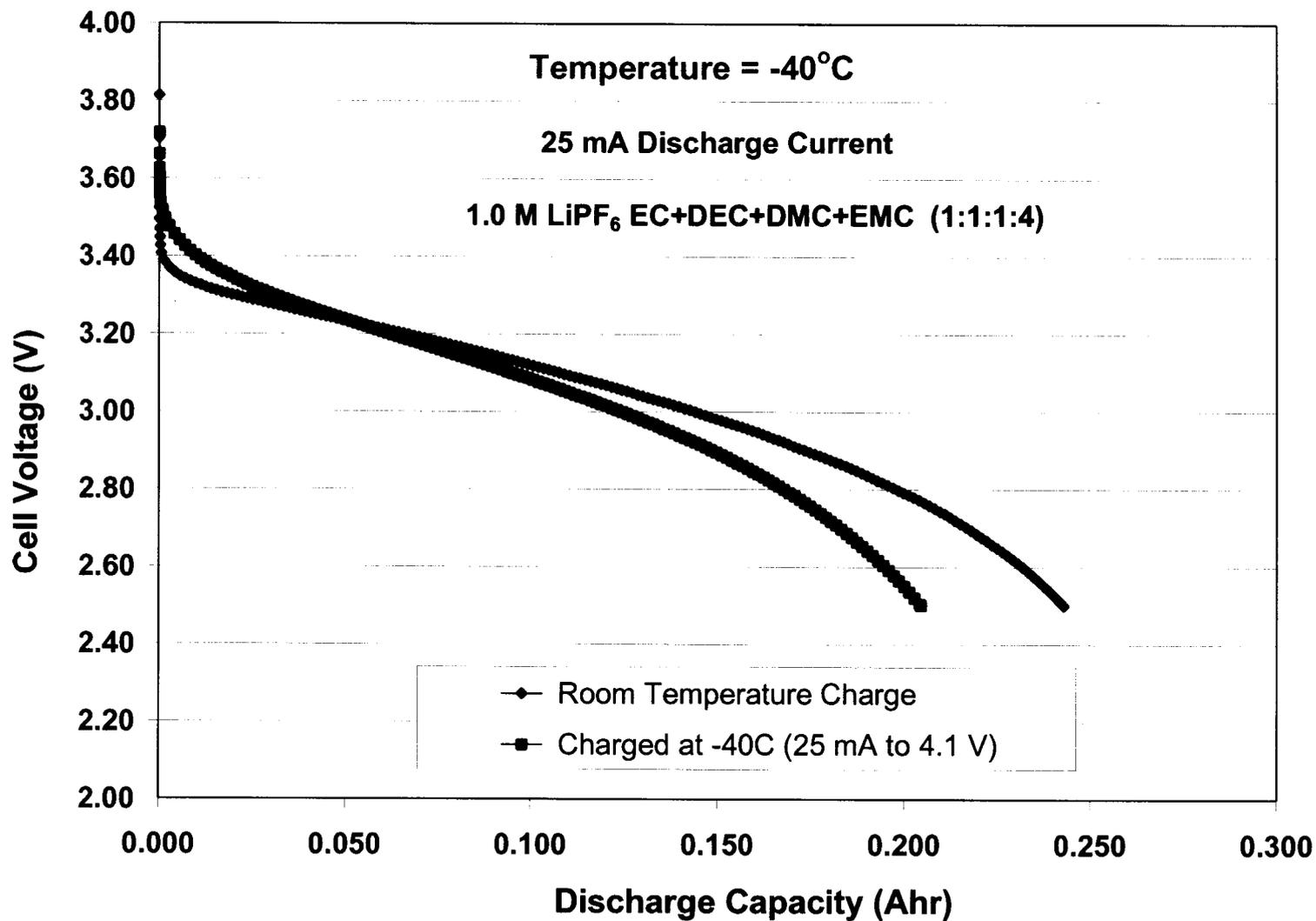


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Charge Characteristics at Low Temperature (- 40°C)





Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Effect of Charging at Low Temperature (-40°C)

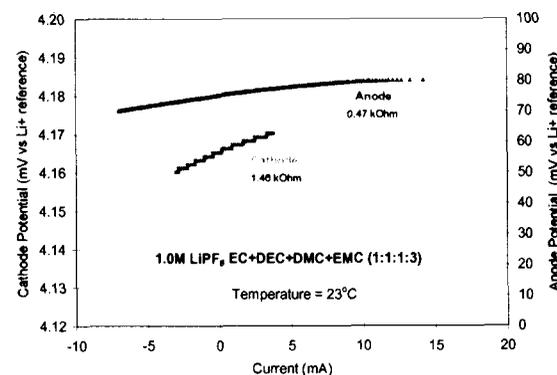




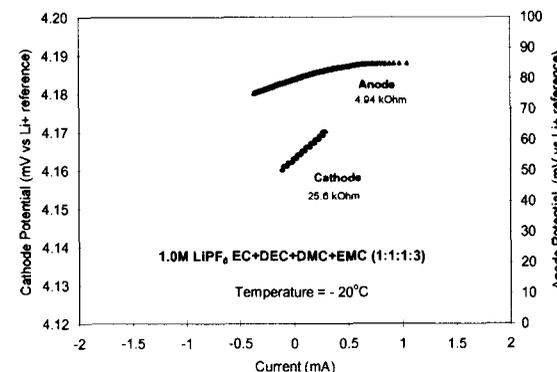
Linear Polarization Measurements

- * At low overpotentials ($\ll RT/\alpha nF$) the electrochemical rate equation can be linearized resulting in a linear current-potential relation.
- * The curves were obtained under potentiodynamic conditions at scan rates of 0.02 mV/sec.
- * The polarization resistance, or the exchange current density, can be calculated from the slopes of the linear plots.
- * The electrodes were tested in near full state of charge and biased over a 10 mV range.
- * The resulting polarization resistance value is indicative of the facility of both the lithium intercalation and de-intercalation processes in the material (encompassing Li^+ diffusion through the SEI layer as well as bulk diffusion in the carbon electrode).

Measurements at 23°C



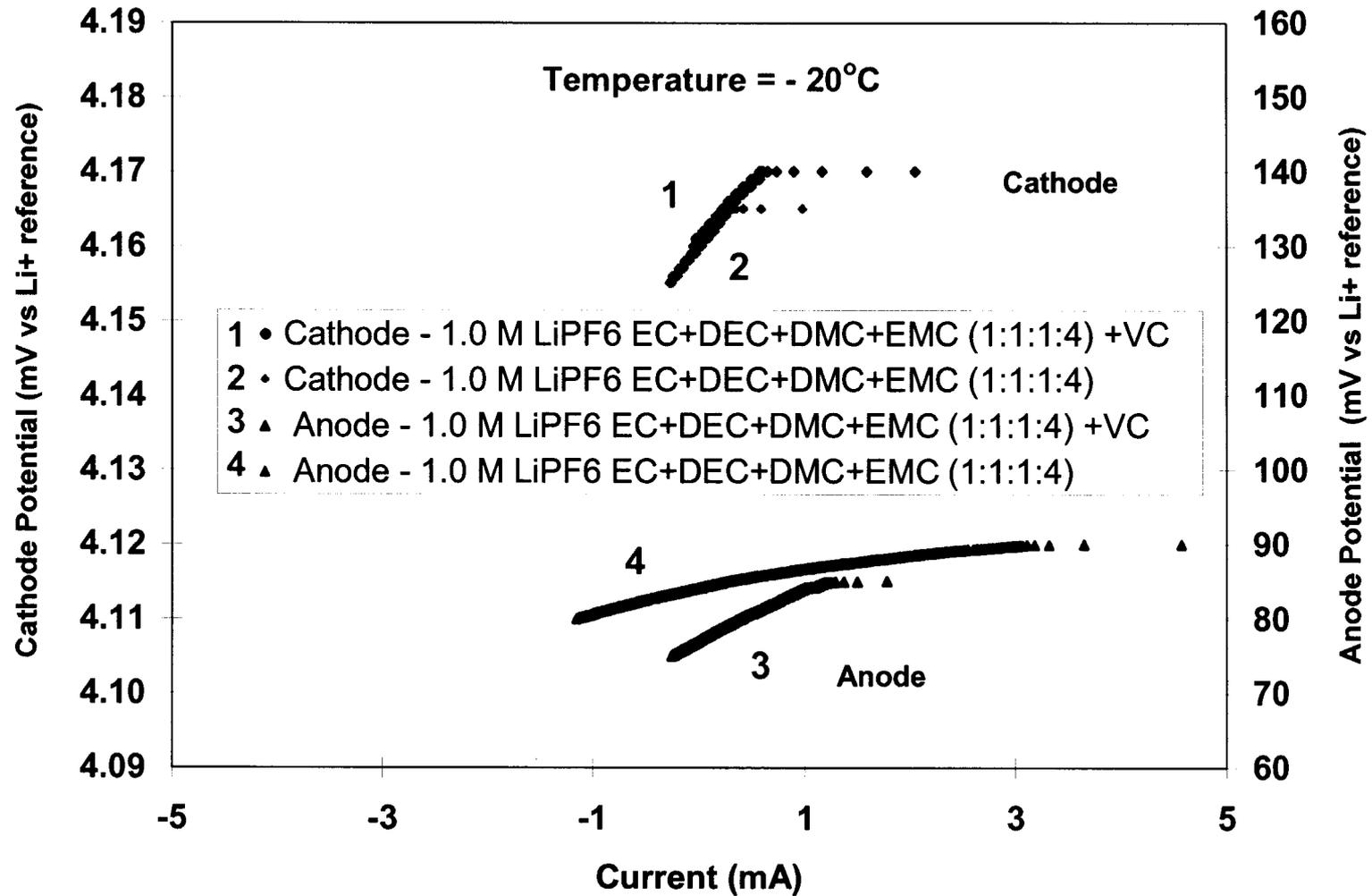
Measurements at - 20°C



- > Polarization resistance is observed to be higher for the cathode with most systems.
- > Good tool to investigate kinetics at different temperatures as a function of electrolyte type

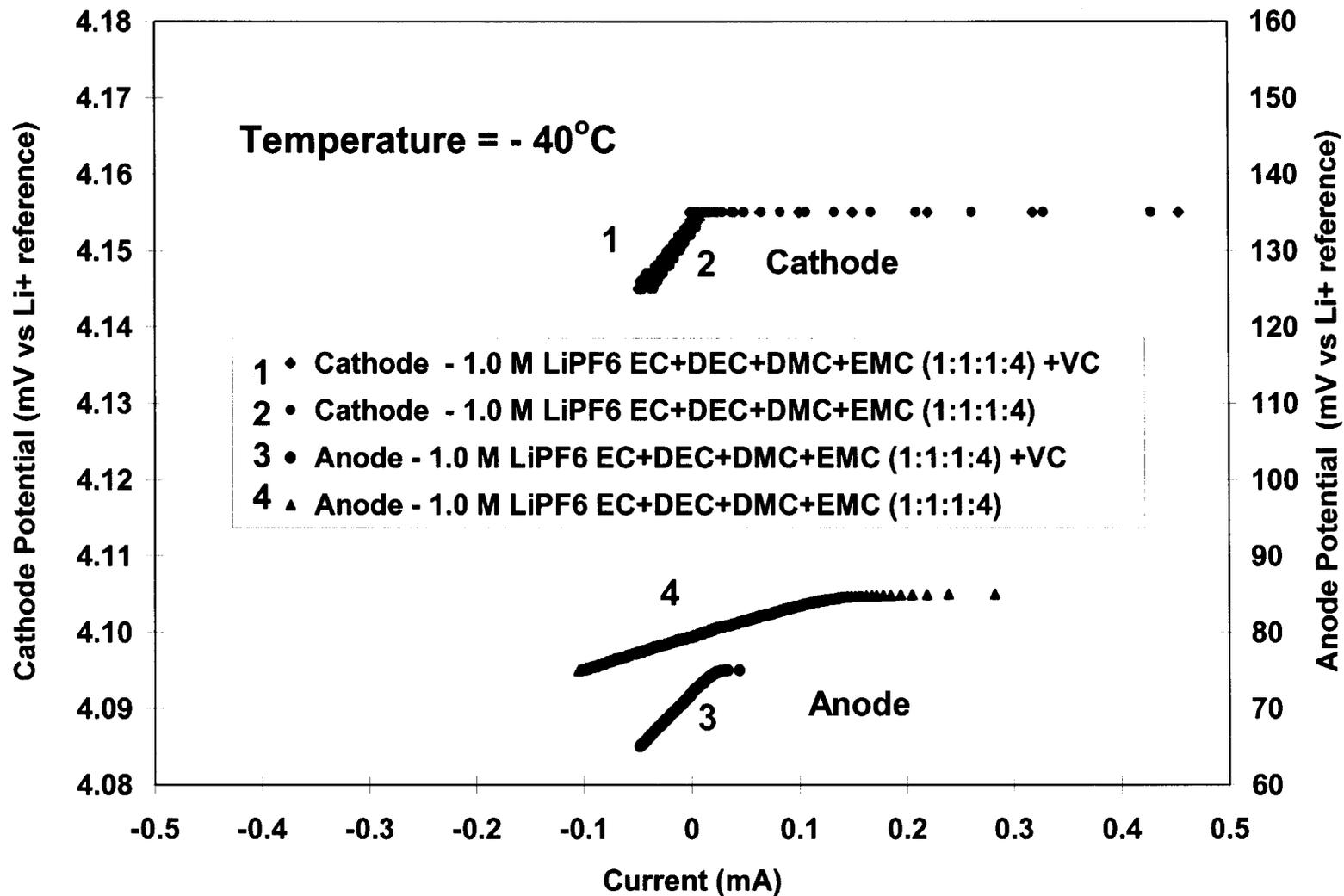


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Linear Micropolarization Measurements at Low Temperature



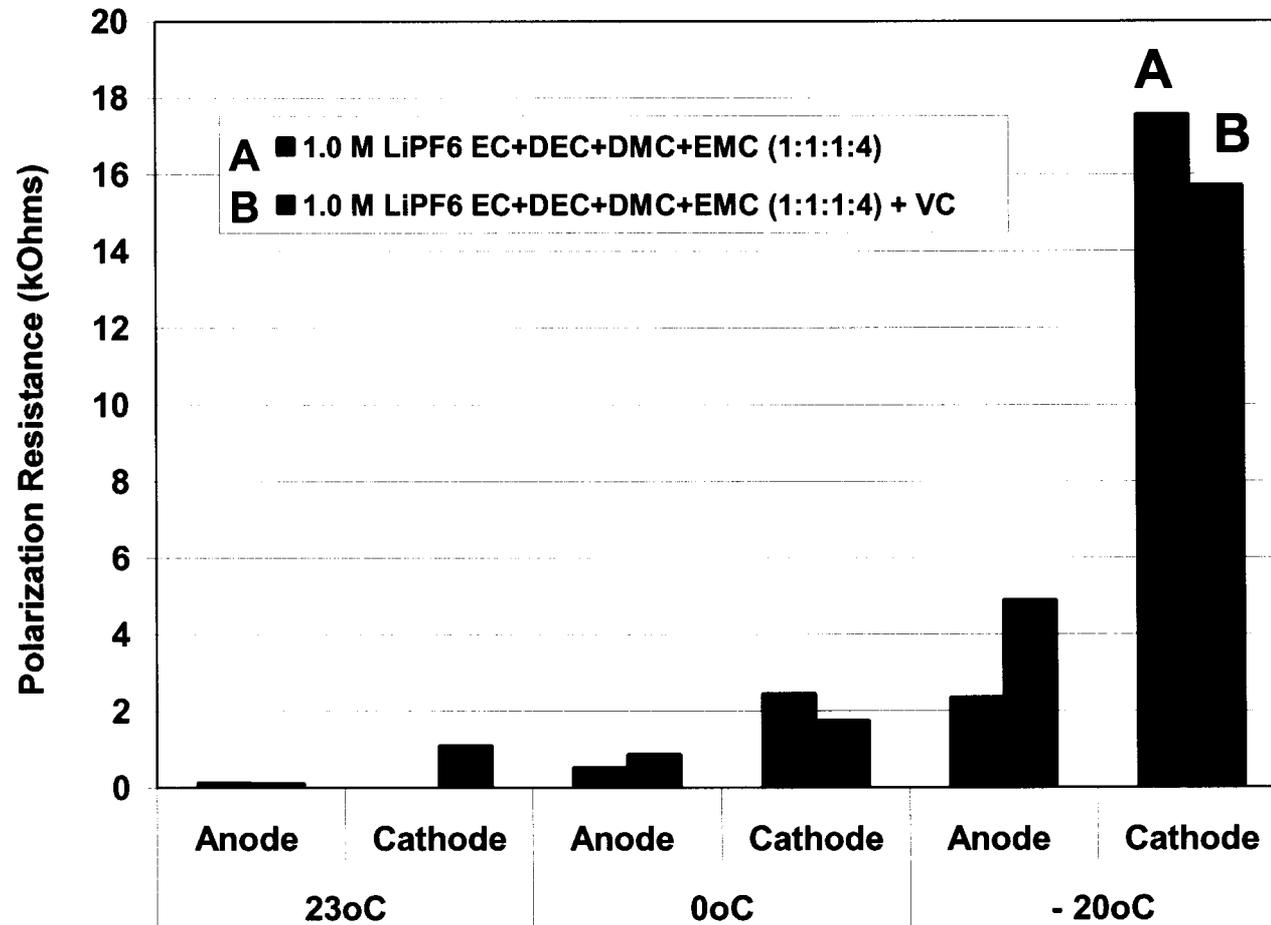


Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Linear Polarization Measurements at Low Temperature





Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Linear Polarization Measurements at Various Temperatures

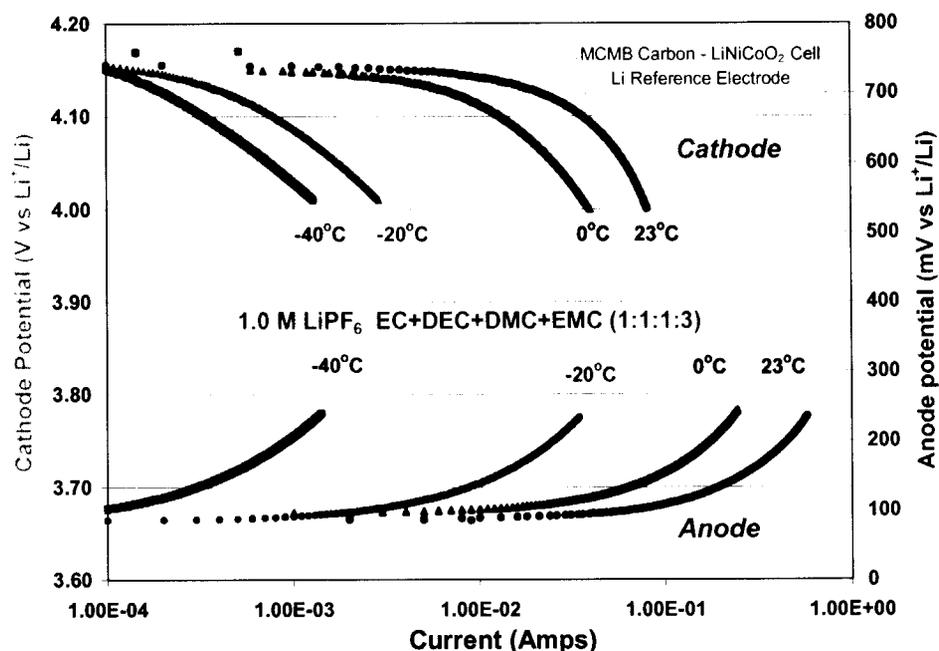


- > At low temperatures, the VC-containing electrolyte results in improved kinetics at the cathode (lower polarization resistance) and poorer lithium kinetics at the anode.



Tafel Polarization Measurements of MCMB and LiNiCoO₂ Electrodes Effect of Electrolyte upon Polarization at Different Temperatures

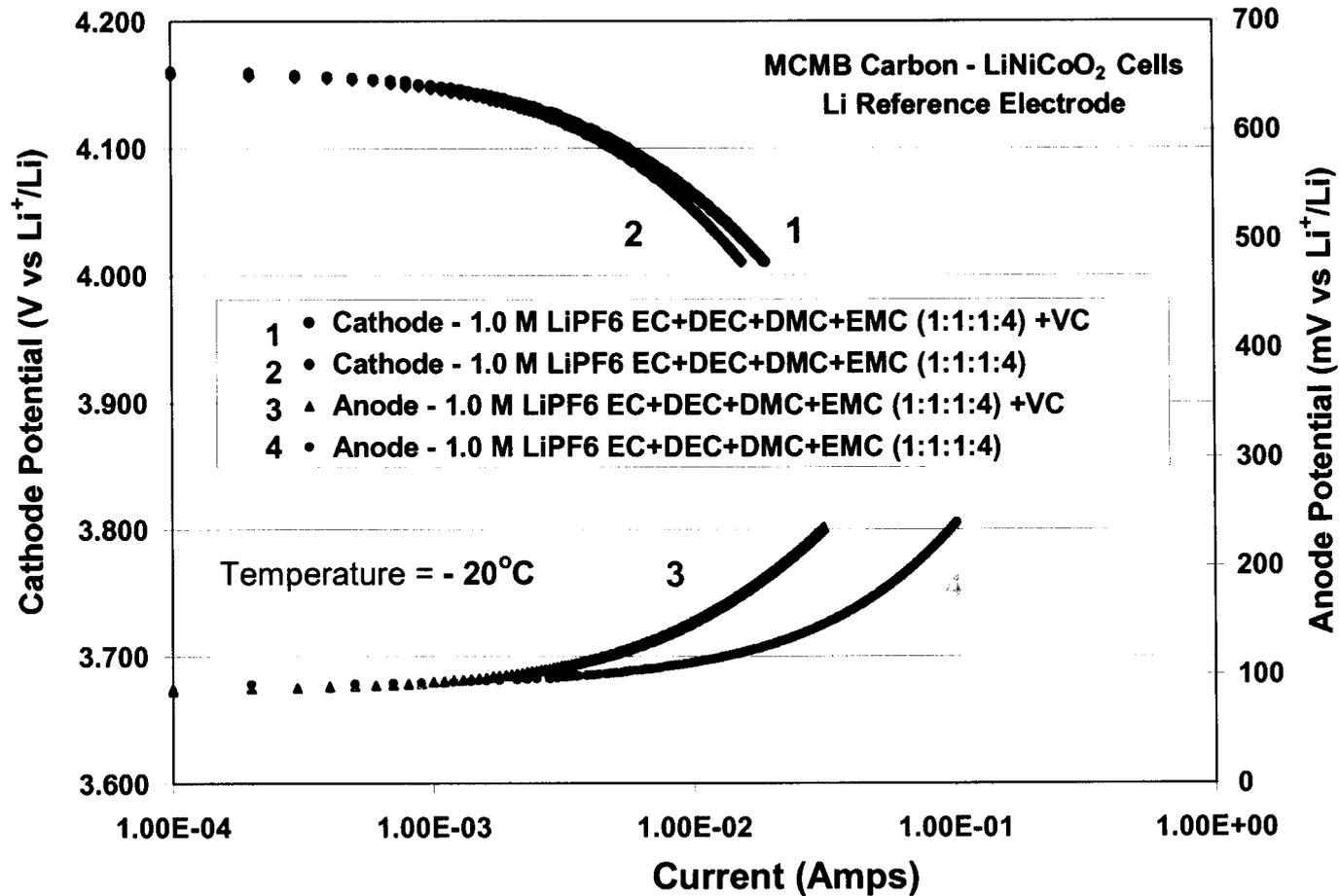
- Tafel polarization measurements allow further insight into the kinetics of lithium intercalation/de-intercalation on MCMB anodes and LiNiCoO₂ cathodes in these electrolytes.
- These measurements were made at scan rates slow enough (0.5 mV/s) to provide near-steady state conditions and yet with minimal changes in the state of charge of the electrode or its surface conditions.
- The cells were tested in near full state of charge and biased over a 150 mV range.
- Both anode and cathode polarization characteristics were measured at various different temperatures (23, 0, - 20 and – 40°C).



- > In most cases, the cathode displays poorer kinetics and is performance limiting.



Effect of Electrolyte Type Upon Electrode Polarization Behavior of Li-Ion Cells: Tafel Polarization Measurements at Low Temperature



- > At low temperatures, the VC-containing electrolyte results in higher cathode electrode limiting current densities and lower anode electrode limiting current densities.



Conclusions

- ***Vinylene carbonate observed to improve low temperature performance***
 - * **Higher discharge capacities observed at -20 and -40°C (RT charge)**

- ***Lithium plating was observed to occur with low temperature charging***
 - * Use of vinylene carbonate in carbonate-based electrolytes shown to result in negative anode potentials under certain condition (high rate charge at low T)
 - * Evidence of Li plating observed with very negative potentials (< -50 mV)
(Especially when potential is not positive at any time during charge)
 - * Increased anode polarization observed to be conducive to plating
 - * Conditions for lithium plating at low temperature are also facilitated if low cathode polarization is observed
 - * In most cases, plating is not observed due greater cathode polarization effects compared to the corresponding anode polarization
 - * A low taper current cut-off on charge is preferred to avoid plating effects

- *Determined that the electrolyte additives can have a profound impact of upon high rate charge and discharge at low temperature and the possibility of lithium plating.*



Conclusions (Continued)

Results of Electrochemical Characterization

- * EIS results indicate that the film and charge transfer resistances are lower for the cell incorporating the VC-containing electrolyte (full cell measurements).
- * Individual electrode measurements indicate that this improvement is primarily attributable to improvements in the cathode electrode properties.
- * Linear micropolarization and Tafel polarization measurements correlate well with the EIS measurements performed and indicate that the cathode kinetics (rather than the anode kinetics) are improved with the addition of VC).

General Observations and Conclusions

- * Although VC may impart many favorable characteristics (protective SEI properties, minimal irreversible loss, good tolerance to high temperature extreme), for improved low temperature performance (including charge at low temperature) the use of VC as an electrolyte additive may not be preferred for all systems.
- This conclusion must be made in the context of all carbonate-based electrolyte which generally result in favorable anode filming properties.
- ***VC appears to have more benefit when coupled with “aggressive” solvents (such as low viscosity ester co-solvents) which otherwise would result in electrode films (especially on the anode) that prove to be highly resistive.***



Acknowledgments

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